Synthesis and spectral properties of 2,7-di-*tert*-butyl-4,9-bis(arylethynyl)- and 4,10-bis(arylethynyl)pyrenes

Jian-yong Hu, Arjun Paudel and Takehiko Yamato*

Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi 1, Saga-shi, Saga 840-8502, Japan

Formylation of 2,7-di-*tert*-butylpyrene with dichloromethyl methyl ether in the presense of $AlCl_3$ afforded a mixture of 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde and 4,10-biscarbaldehyde in the ratio of 75:25, from which the corresponding bis(arylethynyl)pyrenes were obtained by the Wittig reaction with aryl methyl phosphonium ylides followed by bromination and dehydrobromination.

Keywords: pyrenes, Wittig reaction, (phenylethynyl)pyrene, bromination, dehydrobromination

Pyrene and its derivatives have been widely used as fluorescent probes in many applications. For example, pyrene-labelled oligonucleotides have been used as probes to study DNA hybridisation,[1] and pyrene-labelled lipids have been used to study the depth-dependent quenching of fluorescence in lipid bilayers.[2] Recently, the synthesis of a pyrene-based fluorescent dendrimer has been reported wherein the core unit is a 1,3,6,8-tetrasubstituted pyrene and the peripheral units contain monosubstituted pyrene units.[3–5] In the applications of fluorescence techniques, it is desirable to design molecules that have emission in the visible region. The most common method to bathochromically shift the absorption and emission characteristics of a fluorophore to extend the π-conjugation by introducing unsaturated functional groups to the core of the fluorophore.

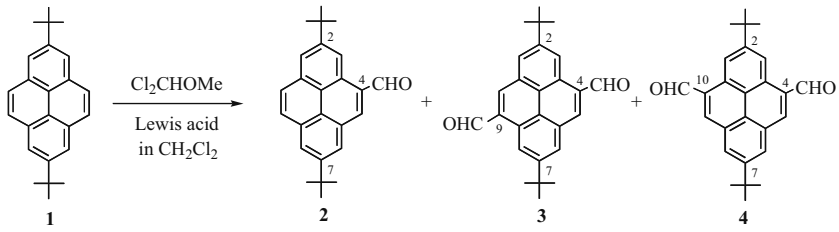
One such group is the acetylenic group. In a recent paper the absorption and fluorescence emission properties of the dimer of 1-ethynylpyrene, namely 1,4-bis(1-pyrene)butadiyne, have been reported,[6] and polymers of 1-ethynylpyrene and 1-trimethylsilylethynylpyrene have been also reported.[7] These polymers exhibit high thermal stability and absorb and emit in the visible region. In the present study, we have used acetylenic groups to extend the conjugation of the pyrene chromophore, Thus there is substantial interest in investigating of the synthesis of arylethynyl substituted pyrenes, and several of its derivatives bearing both hydrophilic and hydrophobic substituents and studies on the electronic absorption and fluoroscence emission properties of these molecules.

We previously reported the $TiCl_4$-catalysed formylation of 2,7-di-*tert*-butylpyrene (**1**) with dichloromethyl methyl ether using the *tert*-butyl group as a positional protective group to afford only 4-monoformylated product, 2,7-di-*tert*-butylpyrene-4-carbaldehyde **2** in excellent yield.[8,9] We have now succeeded in introducing two formyl groups at 4,9 and 4,10 positions. These compounds afforded a convenient starting material for the preparation of the corresponding bis(arylethynyl)pyrenes by the Wittig reaction with aryl methyl phosphonium ylides followed by bromination and dehydrobromination. We report here synthesis and structural properties of novel 4,9- and 4,10-bis(arylethynyl)pyrenes.

Results and discussion

The formylation of 2,7-di-*tert*-butylpyrene **1** with dichloromethyl methyl ether was carried out under the various conditions. Thus, formylation of **1** with dichloromethyl methyl ether at room temperature for 3 h in the presence of titanium tetrachloride occurred selectively at 4-position to afford the corresponding 4-formyl derivative **2** in 93% yield (Table 1). Prolonging the reaction time to 12 h reaction led to the increase of the yield of **2** to 97%. The different regioselectivity was observed in formylation of **1** with dichloromethyl methyl ether (4.0 equiv.) in the presence of $AlCl_3$ for 3 h occurred at 4- and 9- or 10-position to afford a mixture of the corresponding diformylated products **3** and **4** in 35% yield, in which ratio is determined as 74:26 by ^1H NMR spectrum, along with 4-formyl derivative **2** in 65%

Table 1 Formylation of 2,7-di-*tert*-butylpyrene (1) with Cl_2CHOMe.[a]



Run	Lewis acids	Reaction time/h	Product yields/%[b] 2	3	4
1	$TiCl_4$	3	93 [84][c]	0	0
2	$TiCl_4$	12	97 [87][c]	0	0
3	$AlCl_3$	3	65	26	9
4	$AlCl_3$	12	3	73 [55]	24

[a]Yields are determined by G.L.C. analyses. [b]Isolated yields are shown in square parentheses. [c]The starting compound **1** was recovered in 7 and 3% yields, respectively.

* Correspondent. E-mail: yamatot@cc.saga-u.ac.jp

yield. Interestingly, the formylation of **1** with large excess (14.0 equiv.) of dichloromethyl methyl ether in methylene dichloride solution in the presence of $AlCl_3$ for 12 h increased yields of the diformylated derivatives **3** and **4** to 97% in the ratio of 75:25 (^{1}H NMR) along with **2** in 3% yield. The crude product was washed with a hot mixture of hexane-methanol (10 : 1) to furnish the complete separation of **3** in 65% yield as a pale yellow solid, which was recrystallised from hexane afforded pure **3** in 55% yield as pale yellow prisms. However, several attempts to isolate pure **4** failed. The structures of **3** and **4** were assigned by spectral data and elemental analysis. Thus, ^{1}H NMR spectral data (300 MHz, $CDCl_3$) of **3** shows a set of doublets with the *meta*-coupling constant (J = 1.8 Hz) at δ 8.44 ($H_{1,6}$) and 9.92 ($H_{3,8}$) ppm as well as a singlet at δ 8.60 ppm, which is assigned to the protons of positions 5,10 on pyrene ring, respectively. On the other hand, ^{1}H NMR spectral data (300 MHz, $CDCl_3$) of **4** shows three singlets (relative intensity 1:1:1) at δ 8.51 ($H_{6,8}$), 8.57 ($H_{1,3}$) and 9.82 ($H_{5,9}$) ppm and two singlets (relative intensity 1 : 1) at δ 1.62 and 1.64 for *tert*-butyl protons. These data strongly support the assignment of structure of 2,7-di-*tert*-butyl-4,9-diformylpyrene **3** and 2,7-di-*tert*-butyl-4,10-diformylpyrene **4**. These results strongly suggest the *tert*-butyl group on the pyrene ring protects the electrophilic attack at the 1,3,6,8-positions permitting the electrophilic attack at the 4,9 and 4,10-positions.[8,9,10–13] Thus formylation of **1** selectively afforded 4-mono- and 4,9- and 4,10-di-substitution products depending on Lewis acid catalysts used.

The reaction of **3** and the benzyltriphenylphosphonium chloride **5a** with *n*-butyllithium in THF gave the desired (*E,E*)-2,7-di-*tert*-butyl-4,9-bis(2-phenylethenyl)pyrene (*E,E*)-**6a** in 78% yield as a major product, while other possible isomers were not observed (Scheme 1). The *E,E*-isomer (*E,E*)-**6a** was isolated pure by silica gel column chromatography and recrystallisation from hexane. Similarly, (*E,E*)-2,7-di-*tert*-butyl-4,9-bis[2-(4-methoxyphenyl)ethenyl]pyrene (*E,E*)-**6b** was prepared in 82% yield.

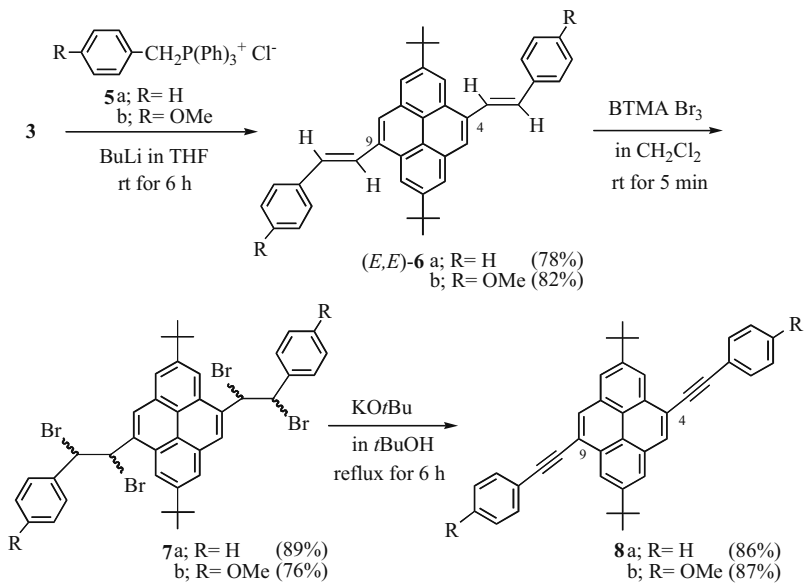
The structures of products *(E,E)*-**6a** and *(E,E)*-**6b** were determined on the basis of their elemental analyses and spectral data. ^{1}H NMR signals of the olefinic protons for *E*-olefins should be observed at lower magnetic field (δ > 7.4 ppm) than that of *Z*-olefins (δ < 6.9 ppm).[14] ^{1}H NMR spectrum of *(E,E)*-**6b** in $CDCl_3$ shows a singlet at δ 3.89 ppm for methoxy protons, a pair of doublets (J = 15.6 Hz) at δ 7.34, 7.92 ppm for olefinic protons, and a pair of doublets (J = 8.7 Hz) at δ 7.01, 7.65 ppm for aromatic protons. These data strongly support that the structure of (*E,E*)-**6b** is the *(E,E)*-configuration.

Attempted bromination of (*E,E*)-**6b** with 2.1 equimolar amounts of benzyltrimethylammonium tribromide (BTMA Br_3), which was recently found to be a convenient solid brominating agent,[15] carried out in a dichloromethane solution at room temperature for 5 min led to the expected *cis* and *trans*-adduct **7b** in the ratio of 20:80 in 76% yield. The same result was obtained from the treatment of (*E,E*)-**6a** with BTMA Br_3 under the same conditions described above.

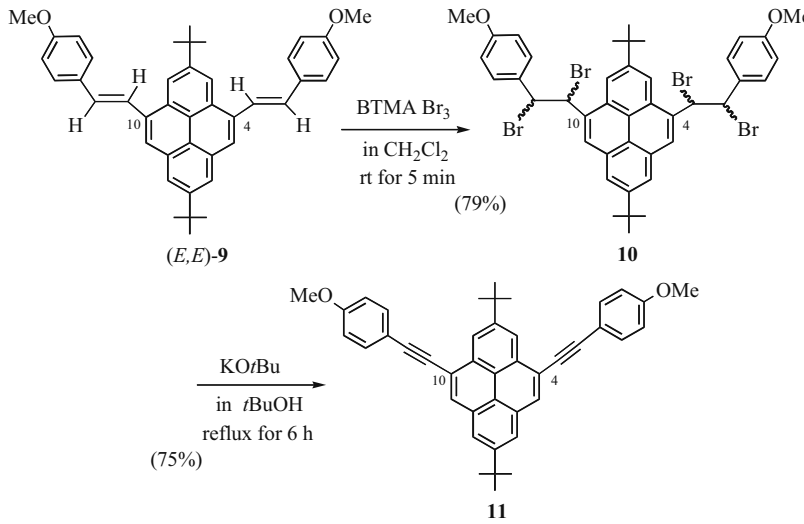
When the bromine adduct **7b** treated with potassium *tert*-butoxide in refluxing *t*BuOH for 6 h, the di-dehydrobromination product 2,7-di-*tert*-butyl-4,9-bis(4-methoxyphenylethynyl)pyrene **8b** was obtained in 87% yield. Similar result was obtained in the case of (*E,E*)-**6a** and the corresponding di-dehydrobromination product, 2,7-di-*tert*-butyl-4,9-bis(4-phenylethynyl)pyrene **8a** was obtained in 86% yield as light-yellow prisms.

Although several attempted isolation of pure 4,10-diformyl compound **4** failed, we have carried out the Wittig reaction of a mixture of **4** and **3** (50 : 50) with (4-methoxybenzyl)triphenylphosphonium chloride **5b** in the presence of *n*-butyllithium in THF to afford a mixture of the desired (*E,E*)-2,7-di-*tert*-butyl-4,10-[2-(4-methoxyphenyl)ethenyl]pyrene (*E,E*)-**9** and 4,9-isomer (*E,E*)-**6b** in 85% yield. Fortunately, we have isolated pure (*E,E*)-**9** by careful column chromatography with ethyl acetate as an eluent. Similarly, we have converted (*E,E*)-**9** to 2,7-di-*tert*-butyl-4,10-bis(4-methoxyphenylethynyl)pyrene **11** by bromination and dehydrobromination (Scheme 2).

The structures of **8a**, **8b** and **11** were determined on the basis of their elemental analyses and spectral data. Thus, IR spectra (KBr) of **8b** shows carbon–carbon triple bond stretching vibration around 2197 cm^{-1}. The similar absorption was observed in **8a** (2195 cm^{-1}) and **11** (2198 cm^{-1}). ^{1}H NMR spectral data (300 MHz, $CDCl_3$) of **8b** shows a set of doublets with the *meta*-coupling constant (J = 1.8 Hz) at δ 8.21 ($H_{1,6}$) and 8.81 ($H_{3,8}$) ppm as well as a singlet at δ 8.35 ppm, which is assigned to the protons of positions 5,10 on pyrene ring,



Scheme 1



Scheme 2

respectively. On the other hand, ^{1}H NMR spectral data (300 MHz, $CDCl_3$) of **11** shows three singlets (relative intensity 1 : 1 : 1) at δ 8.17 ($H_{6,8}$), 8.33 ($H_{1,3}$) and 8.87 ($H_{5,9}$) ppm and two singlets (relative intensity 1 : 1) at δ 1.62 and 1.64 ppm for *tert*-butyl protons. These data strongly support the assignment of structure of 2,7-di-*tert*-butyl-4,9-bis(4-methoxyphenylethynyl)pyrene **8b** and 2,7-di-*tert*-butyl-4,10-bis(4-methoxyphenylethynyl)pyrene **11**.

While the chemical shifts of the ^{1}H and ^{13}C NMR signals arising from both pyrene ring and benzene rings of **8b** are comparable to those of 1,3,6,8,-*tetra*(phenylethynyl)-substituted pyrenes.[5,16] The signals of the acetylenic carbons are observed at δ 86.8 and 94.5 ppm for **8b** in which the latter carbons are in a strongly deshielding region due to the π-electrons of the pyrnene ring like those of 1,8-bis [4-(*N,N*-dimethylamino)phenylethynyl]pyrene (δ 87.0 and 97.2 ppm).[17] Similar findings are also observed in **8a** (δ 88.0 and 94.4 ppm) and **11** (δ 86.7 and 94.3 ppm).

Consequently, we have succeeded to prepare a series of substituted (phenylethynyl)pyrene derivatives **8a, 8b** and **11**. The UV spectra of (phenylethynyl)pyrene derivatives **8a, 8b** and **11** in CH_2Cl_2 along with that of 2,7-di-*tert*-butylpyrene (**1**) are shown in Fig. 1. The spectra were recorded in CH_2Cl_2 in 1×10^{-5} M concentration. For these (phenylethynyl)pyrene derivatives **8a, 8b** and **11**, the spectra are almost identical and three absorption bands were observed in the range of 300–400 nm. The longest wavelength π–π* bands of (phenylethynyl)pyrene derivatives are bathochromically shifted by 35–40 nm in comparison with that of 2,7-di-*tert*-butylpyrene (**1**) due to the introduction of the phenylethynyl group. On the other hand, the increased bathochromic shift of **8b** (*e.g.* 3–4 nm) in comparison with that of **8a** were observed which are ascribed to the increased π-electron density on the benzene ring arising from methoxy group introduced. Interestingly, much larger molar absorptivity was observed in 4,10-bis(phenylethynyl)pyrene derivative **11** in comparison with that in 4,10-bis(phenylethynyl)pyrene derivative **8b**. This finding indicates the higher exciton coupling between two 4-methoxyphenylethynyl at 4,10 positions than that of 4,9-positions.[18–20]

Upon excitation, the emission spectra of bis(phenylethynyl) pyrene derivatives **8a**, **8b** and **11** in CH_2Cl_2 are almost identical and three absorption bands were observed in the range of 390–500 nm. The slightly different shape in the

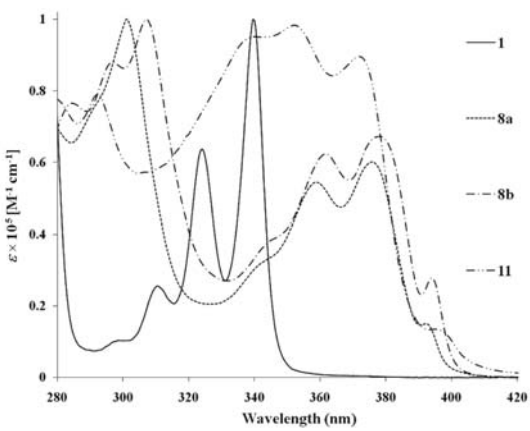


Fig. 1 UV-Vis absorption spectra of compounds **8a**, **8b** and **11** in dichloromethane at 1×10^{-5} M concentration at room temperature, compared with that of compound **1**.

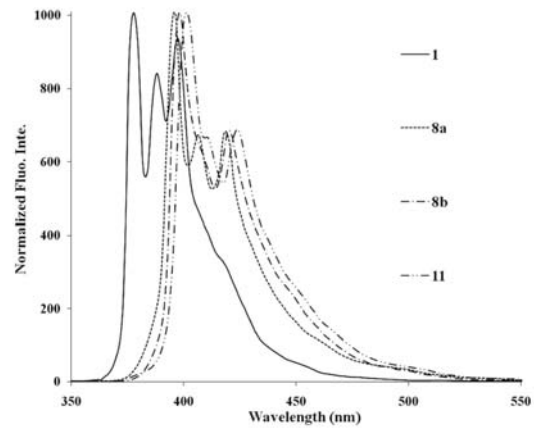


Fig. 2 Emission spectra of compounds **8a**, **8b** and **11** in dichloromethane at 1×10^{-6} M concentration at room temperature, compared with that of compound **1**.

emission spectra of **8a**, **8b** and **11** in comparison with that of **1** are ascribed to the expanded conjugation of π-electron system by the introduction of phenylethynyl groups at the 4,9 and 4,10 positions. Interestingly, the increased bathochromic shift of **8b** (e.g. 3 nm) in comparison with that of **8a** were observed which is in agreement with that of UV-Vis absorption spectra.

Conclusions

We conclude that formylation of 2,7-di-*tert*-butylpyrene with dichloromethyl methyl ether in the presense of $AlCl_3$ afforded a mixture of 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde and 4,10-biscarbaldehyde in the ratio of 75:25, from which the corresponding bis(arylethynyl)pyrenes were obtained by the Wittig reaction with aryl methyl phosphonium ylides followed by bromination and dehydrobromination. Further chemical and structural properties of the present novel bis(arylethynyl)pyrenes derivatives **8** and **11** are currently under study in our laboratory.

Experiment

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. UV-vis spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5.

Materials

Preparation of 2,7-di-*tert*-butylpyrene (**1**) was previously described.[8,9]

Formylation of 2,7-*di-tert-butylpyrene* (**1**) *with* Cl_2CHOMe *in the presence of* $TiCl_4$: To a stirred solution of **1** (5.72 g, 20.0 mmol) and dichloromethyl methyl ether (3.1 mL, 34.4 mmol) in CH_2Cl_2 (200 mL) was added a solution of titanium tetrachloride (5.0 cm^3, 45.5 mmol) in CH_2Cl_2 (100 mL) at 0 °C. This mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (500 mL × 2). The organic layer was washed with water (300 mL × 2), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed over silica gel (Wako, C-300; 200 g) with a toluene as eluent to give a yellow solid, which was recrystallised from hexane–$CHCl_3$ (1 : 1) to afford 2,7-di-*tert*-butylpyrene-4-carbaldehyde **2** (5.95 g, 87%) as yellow prisms, m.p. 175–177 °C (lit[8]. m.p. 175–177 °C).

Formylation of 2,7-*di-tert-butylpyrene* (**1**) *with* Cl_2CHOMe *in the presence of* $AlCl_3$: To a stirred solution of **1** (5 g, 16.0 mmol) and dichloromethyl methyl ether (20 mL, 224 mmol) in CH_2Cl_2 (150 mL) was gradually added a powdered aluminum chloride (13.3 g, 100 mmol) at 0 °C. This mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (300 mL × 2). The organic layer was washed with water (100 mL × 2), dried over $MgSO_4$, and evaporated *in vacuo*. The residue was washed with a hot mixture of hexane-ethyl acetate (5:1) (300 mL × 2) and filtered. The filtrate was concentrated and washed with a hot mixture of hexane-methanol (10:1) (100 mL) to afford the pure 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **3** (3.8 g, 65%) as a yellow solid. Recrystallisation from hexane afforded 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **3** (3.26 g, 55%) as pale yellow prisms, m.p. 246–248 °C; ν_{max}(KBr)/ cm^{-1}: 1680 (C=O); δ_H ($CDCl_3$) 1.63 (18H, s, *t*Bu), 8.44 (2H, d, J = 1.8 Hz, Ar$H_{1,6}$), 8.60 (2H, s, Ar$H_{5,10}$), 9.92 (2H, d, J = 1.8 Hz, Ar$H_{3,8}$) and 10.52 (2H, s, C*H*O); *m/z* 370 (M^+) (Found: C, 84.37; H, 6.99. $C_{26}H_{26}O_2$ (370.5) requires C, 84.29; H, 7.07%).

On the other hand, the filtrate was evaporated to leave the residue which was chromatographed over silica gel (Wako, C-300; 200 g) with a toluene as eluent afforded a mixture of 4,9-di-formyl- (**3**) and 4,10-diformylpyrene (**4**) in which ratio is determined as 50:50 by ^{1}H NMR spectrum. Although several attempted isolations of pure **4** failed, we have used crude **4** for next Wittig reaction.

2,7-di-tert-butylpyrene-4,10-biscarbaldehyde **4**: δ_H ($CDCl_3$) 1.62 (9H, s, *t*Bu), 1.64 (9H, s, *t*Bu), 8.51 (2H, s, Ar$H_{6,8}$), 8.57 (2H, s, Ar$H_{1,3}$), 9.82 (2H, s, Ar$H_{5,9}$) and 10.56 (2H, s, C*H*O).

Typical procedure for Wittig reactions of 2,7-*di-tert-butylpyrene*-4,9-*biscarbaldehyde* (**3**): To a solution of benzyltriphenylphophonium chloride **5a** (2.33 g, 6.0 mmol) in THF (15 mL) was added *n*-BuLi (1.6 M solution in hexane) (3.8 mL, 6.0 mmol) at 0 °C under argon. After the solution was stirred for 10 min, the solution of 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **3** (342 mg, 1.0 mmol) in THF (15 mL) was added. The reaction mixture was stirred at room temperature for 6 h under argon, and then it was poured into a large amount of ice-water and extracted with ethyl acetate (100 mL × 2). The extract was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane-ethyl acetate (5 : 1) as eluent to give (*E,E*)-**6a** as light-yellow solids. Recrystallisation from hexane afforded (*E,E*)-2,7-di-*tert*-butyl-4,9-bis(2-phenyl- ethenyl)pyrene (*E,E*)-**6a** (405 mg, 78%) as light-yellow prisms, m.p. 302–304 °C; δ_H ($CDCl_3$) 1.61 (18H, s, *t*Bu), 7.33–7.49 (6H, m, Ar*H*), 7.44 (2H, d, J = 15.9 Hz, pyrene-CH_b =*CH*$_a$Ar), 7.71 (4H, d, J = 7.2 Hz, Ar*H*), 8.06 (2H, d, J = 15.9 Hz, pyrene-*CH*$_b$ =CH_aAr), 8.27 (2H, d, J = 1.5 Hz, pyrene-$H_{3,8}$), 8.30 (2H, s, pyrene-$H_{5,10}$) and 8.49 (2H, d, J = 1.5 Hz, pyrene-$H_{1,6}$); *m/z* 518 (M +) (Found: C, 92.52; H, 7.43. $C_{40}H_{38}$ (518.75) requires C, 92.62; H, 7.38%).

Similarly, (*E,E*)-**6b** was obtained in 82% yield.

(*E,E*)-2,7-di-*tert*-butyl-4,9-bis[2-(4-methoxyphenyl)ethenyl]pyrene (*E,E*)-**6b** (435 mg, 82%) was obtained as light-yellow prisms, m.p. 229–230 °C; δ_H ($CDCl_3$) 1.61 (18H, s, *t*Bu), 3.89 (6H, s, O*Me*), 7.01 (4H, d, J = 8.7 Hz, Ar*H*), 7.34 (2H, d, J = 15.6 Hz, pyrene-CH_b =*CH*$_a$Ar), 7.65 (4H, d, J = 8.7 Hz, Ar*H*), 7.92 (2H, d, J = 15.6 Hz, pyrene-*CH*$_b$ =CH_aAr), 8.25 (2H, d, J = 1.5 Hz, pyrene-$H_{3,8}$), 8.28 (2H, s, pyrene-$H_{5,10}$) and 8.47 (2H, d, J = 1.5 Hz, pyrene-$H_{1,6}$); *m/z* 578 (M^+) (Found: C, 87.21; H, 7.34. $C_{42}H_{42}O_2$ (578.8) requires C, 87.16; H, 7.31%).

Wittig reactions of 2,7-*di-tert-butylpyrene*-4,10-*biscarbaldehyde* (**4**). To a solution of (4-methoxybenzyl)triphenylphosphonium chloride **5b** (2.53 g, 6.0 mmol) in THF (15 mL) was added *n*-BuLi (1.6 M solution in hexane) (3.8 mL, 6.0 mmol) at room temperature. After the solution was stirred for 10 min, the solution of a mixture of 2,7-di-*tert*-butylpyrene-4,10-biscarbaldehyde **4** and 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde (50 : 50) (370 mg, 1.0 mmol) in THF (15 mL) was added. The reaction mixture was stirred at room temperature for 6 h under argon, and then it was poured into a large amount of ice-water and extracted with ethyl acetate (100 mL × 2). The extract was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane–ethyl acetate (5 : 1) as eluent to give a mixture of (*E,E*)-**9** and (*E,E*)-**6b** (491 mg, 85%) as light-yellow solids. The carefully column chromatography with ethyl acetate as an eluent afforded pure (*E,E*)-2,7-di-*tert*-butyl-4,10-bis[2-(4-methoxyphenyl)ethenyl]pyrene (*E,E*)-**9** (235 mg, 45%) as light-yellow prisms, m.p. 218–220 °C; δ_H ($CDCl_3$) 1.59 (9H, s, *t*Bu), 1.61 (9H, s, *t*Bu), 3.89 (6H, s, O*Me*), 7.00 (4H, d, J = 8.7 Hz, Ar*H*), 7.34 (2H, d, J = 15.9 Hz, pyrene-CH_b =*CH*$_a$Ar), 7.64 (4H, d, J = 8.7 Hz, Ar*H*), 7.92 (2H, d, J = 15.9 Hz, pyrene-*CH*$_b$ =CH_aAr), 8.19 (2H, s, pyrene-$H_{1,3}$) 8.25 (2H, s, pyrene-$H_{6,8}$) and 8.54 (2H, s, pyrene-$H_{5,9}$); *m/z* 578 (M^+) (Found: C, 87.32; H, 7.42. $C_{42}H_{42}O_2$ (578.8) requires C, 87.16; H, 7.31%).

*Typical procedure for bromination of (E,E)-***6** *with BTMA* Br_3. To a solution of *(E,E)*-**6a** (387 mg, 0.75 mmol) in CH_2Cl_2 (40 mL) was added BTMA Br_3 (729 mg, 1.86 mmol) at room temp. After the reaction mixture was stirred at room temp. for 5 min, it was poured into a large amount of ice/water (100 mL) and extracted with CH_2Cl_2 (50 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was recrystallised from hexane gave 560 mg (89%) of a mixture of two diastereomers **7a** and **7a'** in the ratio of 80:20 as colourless prisms, m.p. 200–202 °C; δ_H ($CDCl_3$) **7a**: 1.67 (18H, s, *t*Bu), 6.01 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–*CH*$_a$Br), 6.60 (2H, d, J = 11.4 Hz, pyrene-*CH*$_b$Br–CH_aBr), 7.42–7.47 (2H, m, Ar*H*), 7.51 (4H, d, J = 7.5 Hz, Ar*H*), 7.71 (4H, d, J = 7.5 Hz, Ar*H*), 8.38 (2H, s, pyrene-$H_{1,6}$), 8.52 (2H, s, pyrene-$H_{3,8}$) and 8.47 (2H, d, J = 1.5 Hz, pyrene-$H_{5,10}$); **7a'**: 1.67 (18H, s, *t*Bu), 6.10 (2H, d, J = 12.0 Hz, pyrene-CH_bBr–*CH*$_a$Br), 6.34 (2H, d, J = 11.4 Hz, pyrene-*CH*$_b$Br–CH_aBr), 7.42–7.47 (2H, m, Ar*H*), 7.53 (4H, d, J = 7.5 Hz, Ar*H*), 7.69 (4H, d, J = 7.5 Hz, Ar*H*), 8.27 (2H, s, pyrene-$H_{1,6}$), 8.34 (2H, s, pyrene-$H_{3,8}$) and 8.38 (2H, d, J = 1.5 Hz, pyrene-$H_{5,10}$); *m/z* 837.97 (M^+) (Found: C, 56.92; H, 4.44. $C_{40}H_{38}Br_4$ (838.36) requires C, 57.31; H, 4.57%).

Similarly, a mixture of **7b** and **7b'** was obtained in 76% yield in the ratio of 80:20 as colourless prisms, m.p. 161–163 °C; δ_H ($CDCl_3$)

7b: 1.66 (18H, s, *t*Bu), 3.89 (6H, s, O*Me*), 6.02 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 6.59 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 7.03 (4H, d, J = 7.8 Hz, Ar*H*), 7.64 (4H, d, J = 7.8 Hz, Ar*H*), 8.37 (2H, s, pyrene-$H_{5,10}$), 8.51 (2H, s, pyrene-$H_{3,8}$) and 8.47 (2H, s, pyrene-$H_{1,6}$); **7b'**: 1.66 (18H, s, *t*Bu), 3.89 (6H, s, OMe), 6.09 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 6.35 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 7.03 (4H, d, J = 7.8 Hz, Ar*H*), 7.61 (4H, d, J = 7.8 Hz, Ar*H*), 8.26 (2H, s, pyrene-$H_{5,10}$), 8.33 (2H, s, pyrene-$H_{3,8}$) and 8.37 (2H, s, pyrene-$H_{1,6}$). (Found: C, 56.57; H, 4.71. $C_{42}H_{42}Br_4O_2$ (898.42) requires C, 56.15; H, 4.71%).

Similarly, a mixture of **10 and 10'** was obtained in 79% yield in the ratio of 80:20 as colourless prisms, m.p. 150–152 °C; δ_H ($CDCl_3$) **10**: 1.61 (9H, s, *t*Bu), 1.71 (9H, s, *t*Bu), 3.89 (6H, s, O*Me*), 6.01 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 6.60 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 7.02 (4H, d, J = 8.1 Hz, Ar*H*), 7.64 (4H, d, J = 8.1 Hz, Ar*H*), 8.36 (2H, s, pyrene-$H_{6,8}$), 8.49 (2H, s, pyrene-$H_{1,3}$) and 8.57 (2H, s, Pyrene-$H_{5,9}$); **10'**: 1.57 (9H, s, *t*Bu), 1.66 (9H, s, *t*Bu), 3.89 (6H, s, O*Me*), 6.10 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 6.38 (2H, d, J = 11.4 Hz, pyrene-CH_bBr–CH_aBr), 7.02 (4H, d, J = 8.1 Hz, Ar*H*), 7.63 (4H, d, J = 8.1 Hz, Ar*H*), 8.24 (2H, s, pyrene-$H_{6,8}$), 8.32 (2H, s, pyrene-$H_{1,3}$) and 8.43 (2H, s, pyrene-$H_{5,9}$). (Found: C, 56.47; H, 4.68. $C_{42}H_{42}Br_4O_2$ (898.42) requires C, 56.15; H, 4.71%).

Typical procedure for dehydrobromination of **7a** *and* **7a'** *with KO*t*Bu*. To a solution of a mixture of **7a** and **7a'** (168 mg, 0.20 mmol) in *t*BuOH (24 mL) was added KO*t*Bu (1.34 g, 10.5 mmol) at room temperature. After the reaction mixture was stirred at 80 °C. for 6 h, it was poured into a large amount of ice/water (50 mL) and extracted with CH_2Cl_2 (100 mL × 2). The combined extracts were washed with water, dried with Na_2SO_4 and concentrated. The residue was recrystallised from methanol gave 189 mg (86%) of 2,7-di-*tert*-butyl-4,9-bis(phenylethynyl)pyrene **8a** as light-yellow prisms, m.p. 202–204 °C; ν_{max}(KBr)/cm^{-1}: 2964, 2354, 2195, 1670, 1570, 1460, 1260, 900, 750; δ_H ($CDCl_3$) 1.63 (18H, s, *t*Bu), 7.32–7.46 (6H, m, Ar*H*), 7.33 (4H, d, J = 7.2 Hz, Ar*H*), 8.22 (2H, d, J = 1.5 Hz, pyrene-$H_{3,8}$), 8.38 (2H, s, pyrene-$H_{5,10}$) and 8.83 (2H, d, J = 1.5 Hz, pyrene-$H_{1,6}$); ^{13}C NMR ($CDCl_3$): δ = 149.3, 132.2, 131.7, 130.1, 129.8, 128.6, 123.5, 123.0, 122.3, 121.8, 120.2, 94.4, 88.0, 35.4 and 31.9; *m*/*z*: 514 (M^+) (Found: C, 93.21; H, 6.53. $C_{40}H_{34}$ (514.72) requires C, 93.34; H, 6.66%).

Similarly, compounds **8b** and **11** were obtained in 87% and 75% yields, respectively.

2,7-Di-*tert*-butyl-4,9-bis(4-methoxyphenylethynyl)pyrene **8b** as light-yellow prisms, m.p. 236–238 °C; ν_{max}(KBr)/cm^{-1}: 2953, 2358, 2197, 1610, 1505, 1460, 1280, 1030, 827 and 730; δ_H ($CDCl_3$) 1.62 (18H, s, *t*Bu), 3.89 (6H, s, O*Me*), 6.99 (4H, d, J = 8.7 Hz, Ar*H*), 7.67 (4H, d, J = 8.7 Hz, Ar*H*), 8.21 (2H, d, J = 1.5 Hz, pyrene-$H_{3,8}$), 8.35 (2H, s, pyrene-$H_{5,10}$) and 8.81 (2H, d, J = 1.5 Hz, pyrene-$H_{1,6}$); ^{13}C NMR ($CDCl_3$): δ = 159.8, 149.6, 133.2, 130.9, 130.2, 122.9, 122.2, 121.8, 120.2, 115.6, 114.3, 94.5, 86.8, 55.4, 35.4 and 32.0; *m*/*z* 574 (M^+) (Found: C, 87.63; H, 6.62. $C_{42}H_{38}O_2$ (574.77) requires C, 87.77; H, 6.66%).

2,7-Di-*tert*-butyl-4,10-bis(4-methoxyphenylethynyl)pyrene **11** as light-yellow prisms, m.p. 224–226 °C; ν_{max}(KBr)/cm^{-1}: 2958, 2356, 2198, 1620, 1508, 1460, 1270, 1030 and 830; δ_H ($CDCl_3$) 1.58 (9H, s, *t*Bu), 1.68 (9H, s, *t*Bu), 3.88 (6H, s, O*Me*), 6.99 (4H, d, J = 8.7 Hz, Ar*H*), 7.67 (4H, d, J = 8.7 Hz, Ar*H*), 8.17 (2H, s, pyrene-$H_{6,8}$), 8.33 (2H, s, pyrene-$H_{1,3}$) and 8.87 (2H, s, pyrene-$H_{5,9}$); ^{13}C NMR ($CDCl_3$): δ = 159.8, 149.3, 149.1, 133.2, 132.5, 131.5, 130.9, 128.8, 122.9, 121.6, 120.8, 115.7, 114.3, 94.4, 86.9, 55.4, 35.6, 35.2, 32.1 and 31.9; *m*/*z* 574 (M^+) (Found: C, 87.83; H, 6.68. $C_{42}H_{38}O_2$ (574.77) requires C, 87.77; H, 6.66%).

Received 14 October 2008; accepted 5 December 2009
Paper 08/0206 *doi: 10.3184/030823409X401295*
Published online: 24 February 2009

References

1 J.R. Lakowicz, *Principles of fluorescence spectroscopy*, 2nd ed., Kluwer Academic/Plenum Publishers, New York, 1999, ch. 21, pp, 595–614.
2 M. Sussaroli, M. Ruonala, J. Virtanen, M. Vauhkonen and P. Somerharju, *Biochemistry*, 1995, **34**, 8843.
3 C. Modrakowski, S.C. Flores, M. Beinhoff and A.D. Schlüter, *Synthesis*, 2001, 2143.
4 M. Beinhoff, W. Weigel, M. Jurczok, W. Rettig and A.D. Schlüter, *Eur. J. Org. Chem.*, 2001, 3819.
5 G. Venkataramana and S. Sankararaman, *Eur. J. Org. Chem.*, 2005, 4162.
6 A.C. Benniston, A. Harriman, D.J. Lawrie and S.A. Rostron, *Eur. J. Org. Chem.*, 2004, 2272.
7 E. Rivera, M. Belletete, X.X. Zhu, G. Durocher and R. Giasson, *Polymer*, 2002, **43**, 5059.
8 T. Yamato, A. Miyazawa and M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, 1993, 3127.
9 T. Yamato and J. Hu, *J. Chem. Res*, 2006, 762.
10 T. Yamato, A. Miyazawa and M. Tashiro, *Chem. Ber.*, 1993, **126**, 2501.
11 T. Yamato, M. Fujimoto, A. Miyazawa and K. Matsuo, *J. Chem. Soc. Perkin Trans. 1*, 1193 (1997).
12 T. Yamato, M. Fujimoto, Y. Nagano, A. Miyazawa and M. Tashiro, *Org. Prep. Proc. Int.*, **29**, 321-330 (1997).
13 J. Hu, A. Paudel and T. Yamato, *J. Chem. Res.*, 2008, 308.
14 A. Merz, A. Karl, T. Futterer, N. Stacherdinger, O. Schneider, J. Lex, E. Lubochand and J.F. Biernat, *Liebigs Ann. Chem.*, 1994, 1199.
15 S. Kajigaeshi, T. Kakinami, H. Tokiyama, T. Hirakawa and T. Okamoto, *Chem. Lett.*, 1987, 627.
16 G. Venkataramana and S. Sankararaman, *Org. Lett.*, 2006, **8**, 2739.
17 H.M. Kim, Y.O. Lee, C.S. Lim, J.S. Kim and B.R. Cho, *J. Org. Chem.*, 2008, **73**, 5127.
18 J.S. Melinger, Y. Pan, V.D. Kleiman, Z. Peng, B.L. Davis, D. McMorrow and M. Lu, *J. Am. Chem. Soc.*, 2002, **124**, 12002.
19 F.D. Lewis, R.S. Kalgutkar and J.-S. Yang, *J. Am. Chem. Soc.*, 1999, **121**, 12045.
20 J. Yang, Y. Lee, J. Yan and M. Lu, *Org. Lett.*, 2006, **8**, 5813.